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POROUS MATERIAL AND PRODUCTION PROCESS THEREOF

This application is a continuation of International Application No. PCT/JP03/02999, filed on March 13, 2003, which claims the benefit of Japanese Patent Application Nos. 2002-073111, filed on March 15, 2002 and 2002-363164, filed on December 13, 2002.

10 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a porous material and a production process thereof.

Related Background Art

15 Much attention has recently been paid to microstructures as functional materials. Techniques for producing such microstructures include a technique for directly manufacturing a microstructure by semiconductor processing technology typified by  
20 pattern forming technology such as photolithography (refer to JP 5-55545 A).

Besides the above semiconductor processing technology, there is a technique making use of the self-organization phenomenon or self-formation  
25 phenomenon of a material. That is, a novel microstructure is to be realized based on a naturally formed regular structure.

## SUMMARY OF THE INVENTION

Since the technique making use of the self-organization or self-formation phenomenon has the potential of ~~realizing~~ *producing* not only a micron-scale structure, but also a nano-scale structure, many ~~researches have been made on the technique.~~ *this technique has been explored in* However, it cannot be said that the technique has been completely established, and ~~provision of a novel microstructure and the establishment of its~~ *are still* production process ~~have been~~ desired.

It is therefore an object of the present invention to provide a novel structure and a production process thereof.

According to an aspect of the present invention, there is provided a porous material comprising a plurality of columnar pores and an area that surrounds the pores, wherein <sup>2</sup> the area is an amorphous area containing C, Si, Ge or a combination thereof.

It is preferable that the columnar pores are substantially unbranched.

It is preferable that the average interval between the centers of adjacent pores is 30 nm or less, and that the diameter of each of the columnar pores is 20 nm or less.

Further, it is preferable that the plurality of pores have substantially the same depth direction.

Note that the area may contain aluminum.

Note that when the porous material is formed on a substrate, there is obtained a porous material in which the depth directions of the columnar pores are substantially perpendicular to the substrate.

Further, according to another aspect the present invention, there is provided a porous material obtained by removing a first material from a structure including the first material and a second material, wherein the structure has columnar members containing the first material and surrounded by an amorphous area containing the second material, and that the structure contains the second material in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material.

The first material is aluminum, for example. The second material is, for example, Si, Ge, SiGe, C or a combination thereof.

Further, according to another aspect of the present invention, there is provided a process for producing a porous material comprising the steps of: preparing a structure which contains a first material and a second material and has columnar members containing the first material and surrounded by an area containing the second material; and removing the columnar members from the structure.

Here, it is preferable that the structure

contains the second material in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material.

The diameters of pores formed by the removing step may be ~~expanded~~ <sup>increased</sup> after the removing step.

Further, according to another aspect of the present invention, there is provided a process for producing a porous material comprising the steps of: preparing a structure which contains aluminum and silicon, has columnar members containing aluminum and a silicon area surrounding the columnar members, and contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon; and removing the columnar members from the structure.

The silicon area may contain germanium.

The use of the above porous material permits provision of a filter or a mask.

Further, according to yet another aspect of the present invention, there is provided a porous material having columnar pores and an area surrounding the pores, wherein the average diameter of the pores is 20 nm or less and the average interval between the pores is 30 nm or less.

Further, according to still another aspect of the present invention, there is provided a process for producing a porous material comprising the steps of: preparing a structure which contains a first

material and a second material and has columnar members containing the first material and surrounded by an area containing the second material, and which contains the second material in an amount of 20 to 70  
5 atomic% based on the total amount of the first material and the second material; and removing the columnar members from the structure.

According to still another aspect of the present invention, there is provided a porous  
10 material comprising columnar pores and an area<sup>✓</sup> surrounding the pores, in which a first material (for example, aluminum) is contained in the area in an amount of 1 to 20% based on the total amount of the first material and a second material. The ~~unit is~~ *unit is umtsare*  
15 atomic%.

The above amount is the amount of aluminum contained in a Si porous material when the first material is aluminum and the second material is silicon. *This* ~~The amount~~ does not include the amount of  
20 oxygen contained in the porous material.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are schematic diagrams of a porous material according to the present invention;

25 Figs. 2A, 2B and 2C are diagrams for explaining an example of a process for producing a porous material according to the present invention;

Fig. 3 is a diagram for explaining an example of a process for producing a porous material according to the present invention;

Figs. 4A, 4B, 4C and 4D are diagrams for explaining an example of a process for producing a porous material according to the present invention;

Fig. 5 is a schematic diagram showing a film forming process for the structure of the present invention; and

Fig. 6 is a schematic diagram of a porous material according to the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will <sup>now</sup> be described in detail ~~hereinunder~~.

*Initially, a* description is ~~first given~~ <sup>provided</sup> of a structure ~~applicable to~~ <sup>for use in</sup> the present invention.

(1) Structure ~~applicable to~~ <sup>for use in</sup> the present invention

The structure ~~applicable to~~ <sup>for use in</sup> the present invention includes a first material and a second material, in which <sup>structure</sup> columnar members containing the first material are surrounded by an area containing the second material ~~and~~ <sup>The</sup> second material ~~is contained in the structure in an amount of~~ <sup>comprises</sup> 20 to 70 atomic% ~~based on~~ <sup>of</sup> the total amount of the first material and the second material. A porous material according to the present invention is obtained by

removing the above columnar members from this structure. When the porous material is left in an atmosphere including oxygen <sup>such</sup> ~~as the~~ <sub>in</sub> air, an oxide area is readily formed on the surface layer (the surface of a film or the wall of each pore) of the porous material.

The above amount refers to the amount of the second material based on the total amount of the first material and the second material forming the structure. It is preferably 25 to 65 atomic%, more preferably 30 to 60 atomic%.

<sup>When a</sup> ~~A~~ substantially columnar form needs to be obtained, the second material may be contained as a component of the columnar members, and the first material (for example, aluminum, <sup>below</sup> ~~as will be described hereinafter~~) may be contained in the above area. Oxygen, argon and the like may be contained in the above columnar members and the area surrounding the members.

The above amount is determined, for example, by inductive coupled plasma emission spectral analysis. The unit of atomic% is used. When the unit of wt% is used, 20 to 70 atomic% is equivalent to 20.65 to 70.84 wt% (the atomic weight of Al is 26.982 and the atomic weight of Si is 28.086).

Examples of the first material include Al, Au, Ag and Mg. Examples of the second material include

Si, Ge,  $\text{Si}_x\text{Ge}_{1-x}$  and C. The second material is particularly preferably a material which can be amorphous. The first material and the second material are preferably a material<sup>s</sup> (so-called  
5 eutectic material<sup>s</sup> having <sup>a</sup> eutectic temperature in the phase diagrams of ~~the~~ both components. The eutectic temperature is 300°C or higher, preferably 400°C or higher. A eutectoid material may also be used. A preferred combination of the first material  
10 and the second material includes that in which Al is used as the first material and Si is used as the second material, in which Al is used as the first material and Ge is used as the second material, or in which Al is used as the first material and  $\text{Si}_x\text{Ge}_{1-x}$  ( $0$   
15  $< x < 1$ ) is used as the second material. The amount of the first material (for example, aluminum) contained in the above area forming the above porous material is preferably 1 to 20 atomic%. This amount refers to the amount of aluminum contained in the Si  
20 porous material when the first material is aluminum and the second material is silicon. This amount does not include the amount of oxygen contained in the porous material.

The area surrounding the above columnar members  
25 is desirably amorphous.

The plane form of each columnar member is circular or oval.



The above structure has a plurality of the above columnar members dispersed in a matrix containing the second material. The size (diameter when the plane form is circular) of each columnar member can be controlled mainly by the composition (that is, the amount of the second material) of the above structure. The average diameter of the columnar members is 0.5 to 50 nm, preferably 0.5 to 20 nm, more preferably 0.5 to 10 nm. The diameter is represented by  $2r$  in Fig. 1B. When the plane form is oval or the like, the longest outer diameter needs to be within the above range. The average diameter is obtained from the actual SEM photo (about 100 nm  $\times$  100 nm) of the columnar portions directly or after processing the image <sup>using</sup> ~~with~~ a computer. The lower limit of the average diameter, which depends on which device the above structure is used for or ~~which~~ <sup>how</sup> ~~processing is made on~~ the structure, <sup>is processed</sup> ~~is~~ 1 nm or several nanometers from the viewpoint of practical use.

The interval  $2R$  between the centers of adjacent columnar members (Fig. 1B) is 2 to 30 nm, preferably 5 to 20 nm, more preferably 5 to 15 nm. ~~It is needless to say that~~ the lower limit of the interval  $2R$  must be such that the columnar members do not contact ~~with~~ each other.

Preferably, the above pore diameter is 20 nm or

less and the interval between the centers of adjacent pores is 30 nm or less.

The above structure is preferably a film-like structure. In this case, the above columnar members  
5 are dispersed in the matrix containing the second material in such a manner that they are substantially perpendicular to the plane direction of the film. The thickness of the film-like structure is not particularly limited, but <sup>is</sup> suitably 1 nm to 100  $\mu$ m. In  
10 consideration of the process time and the like, the practical thickness of the film is 1 nm to 1  $\mu$ m. It is preferred that even when the thickness of the film is 300 nm or more, columnar structures be maintained. The columnar members are columnar structures having  
15 substantially no branches in the thickness direction.

The above structure is preferably a film-like structure and may be formed on a substrate. The substrate is not particularly limited. Examples of the substrate include insulating substrates made from  
20 quartz glass or the like, <sup>a</sup> silicon substrate, semiconductor substrates made from gallium arsenide or indium phosphide, metal substrates made from aluminum or the like, and flexible substrates (made from <sup>a</sup> polyimide resin or the like) as support members  
25 on which the above structure can be formed. The above columnar members are formed <sup>to be</sup> substantially perpendicular to the substrate.

The above structure can be manufactured by using a process for forming a film under a non-equilibrium condition. The above film forming process is preferably sputtering, but any film forming process for forming a substance under a non-equilibrium condition can be used, such as resistance heating deposition, electron beam deposition (EB deposition) or ion plating. <sup>For</sup> ~~When sputtering is used,~~ magnetron sputtering, RF sputtering, ECR sputtering or DC sputtering may be used. ~~When sputtering is~~ used <sup>stet</sup>, film formation can be carried out by setting the inside pressure of a reactor to 0.2 to 1 Pa in an argon atmosphere. For sputtering, the above first material and second material may be prepared separately as target raw materials, or a target material obtained by baking in advance the first material and the second material at a desired ratio may be used. Sputtering is preferably carried out <sup>under such</sup> ~~in~~ ~~the~~ <sup>the</sup> conditions, that plasma does not substantially contact ~~with a~~ <sup>the</sup> substrate from which the above structure grows.

The above structure is desirably formed on the substrate at a substrate temperature of 20 to 300°C, preferably 20 to 200°C, more preferably 100 to 150°C.

A porous material having a plurality of columnar pores is formed by removing (wet etching or dry etching) the above columnar members from the

above structure. Etching is used to selectively remove the columnar members, and the etchant is preferably an acid, such as phosphoric acid, sulfuric acid, hydrochloric acid or nitric acid. The pores of  
5 the porous material formed by removing the columnar members are preferably not connected to one another, but <sup>are</sup> independent ~~from one another~~. The plurality of the formed pores have the same depth direction.

When the porous material is exposed to an  
10 atmosphere (liquid or gas) containing oxygen, an oxide area is readily formed on the wall of each pore. Therefore, an oxide area may be positively formed on the wall of each pore of the porous material.

(2) A description is subsequently <sup>provided</sup> ~~given~~ of the  
15 ratio of the first material (forming the columnar members) to the second material (forming the area surrounding the columnar members) in the structure applicable <sup>for use in</sup> ~~to~~ the present invention.

The reason why the porous material of the  
20 present invention can be provided is that the following structure could be obtained by intensive efforts made by the inventors of the present invention.

An aluminum-silicon mixed film which contained  
25 silicon in an amount of 55 atomic% based on the total amount of aluminum and silicon was formed on a glass substrate 11 to a thickness of about 200 nm by RF

magnetron sputtering. As shown in Fig. 5, a 4-inch aluminum target having eight 15 mm-square silicon chips 13 mounted thereon was used as a target. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa, and the input power was 1 kW. The substrate temperature was room temperature.

The aluminum target as the target 12 had eight silicon chips 13 mounted thereon. The number of silicon chips is not limited to 8 and may change according to sputtering conditions if the ~~content of~~ <sup>content</sup> silicon in the aluminum-silicon mixed film is about 55 atomic%. The target is not limited to an aluminum target having silicon chips mounted thereon and may be a silicon target having aluminum chips mounted thereon or a target obtained by sintering silicon and aluminum powders.

The thus obtained aluminum-silicon mixed film was analyzed by ICP (inductive coupled plasma emission spectral analysis) to measure the amount (atomic%) of silicon based on the total amount of silicon and aluminum. As a result, the amount of silicon was about 55 atomic% based on the total amount of silicon and aluminum. For the convenience of measurement, an aluminum-silicon mixed film deposited on a carbon substrate was used as a substrate.

The aluminum-silicon mixed film was observed through an FE-SEM (field emission scanning electron microscope). Circular aluminum nano-structures surrounded by silicon were arranged two-dimensionally.

- 5 The diameter of each aluminum nano-structure portion was 3 nm and the average interval between the centers of adjacent nano-structure portions was 7 nm. When the section of each nano-structure portion was observed through FE-SEM, the height thereof was 200  
10 nm and the aluminum nano-structure portions were independent from one another.

When this specimen was observed by an X-ray diffraction method, a peak showing the crystallinity of silicon could not be observed and silicon was  
15 amorphous. A plurality of peaks showing the crystallinity of aluminum could be seen, which means that at least <sup>a</sup>part of aluminum was <sup>a</sup>polycrystal.

Accordingly, an aluminum silicon nano-structure containing aluminum nano-cylinder surrounded by  
20 silicon and having an interval  $2R$  of 7 nm, a diameter  $2r$  of 3 nm and a height  $L$  of 200 nm could be manufactured.

Thus, the inventors of the present invention have found that an aluminum-silicon nanostructure  
25 having aluminum nano-structure, such as aluminum quantum dots or aluminum quantum wires having a scale of several nanometers in a silicon matrix on the

surface of a substrate, is manufactured by forming an aluminum-silicon mixed film in accordance with a film forming process for forming a substance under a non-equilibrium condition, such as sputtering.

5 *g* Comparative Example *g*

As a comparative specimen A, an aluminum-silicon mixed film which contained 15 atomic% of silicon based on the total amount of aluminum and silicon was formed on a glass substrate to a  
10 thickness of about 200 nm by sputtering. A 4-inch aluminum target having two 15 mm-square silicon chips 13 mounted thereon was used as a target. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge  
15 pressure was 0.7 Pa, and the input power was 1 kW. The substrate temperature was room temperature.

The comparative specimen A was observed through FE-SEM (field emission scanning electron microscope). When the surface of the specimen was ~~seen~~ <sup>examined</sup> from above  
20 the substrate, aluminum portions were not circular and were continuously connected to one another. That is, a microstructure in which aluminum columnar structures were uniformly dispersed in a silicon area was not obtained. The size of each aluminum columnar  
25 structure was much larger than 10 nm. When the section of the structure was observed through FE-SEM, the width of the aluminum portion was larger than 15

nm. The thus obtained aluminum-silicon mixed film was analyzed by ICP (inductive coupled plasma emission spectral analysis) to measure the amount (atomic%) of silicon based on the total amount of aluminum and silicon. As a result, the amount of silicon was about 15 atomic% based on the total of aluminum and silicon.

Further, an aluminum-silicon mixed film containing silicon in an amount of 75 atomic% based on the total amount of aluminum and silicon was formed on a glass substrate to a thickness of about 200 nm by sputtering as a comparative specimen B. A 4-inch aluminum target having fourteen 15 mm-square silicon chips 13 mounted thereon was used as a target. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa, and the input power was 1 kW. The substrate temperature was room temperature.

The comparative specimen B was observed through FE-SEM (field emission scanning electron microscope). When the surface of the specimen was ~~seen~~<sup>examined</sup> from above the substrate, aluminum portions could not be observed. Even when the section of the specimen was observed through FE-SEM, the aluminum portions could not be clearly observed. The thus obtained aluminum-silicon mixed film was analyzed by ICP (inductive coupled plasma emission spectral analysis) to measure



the amount (atomic%) of silicon based on the total amount of silicon and aluminum. As a result, the amount of silicon was about 75 atomic% based on the total amount of silicon and aluminum.

5        Specimens which contained silicon in amounts of 20 atomic%, 35 atomic%, 50 atomic%, 60 atomic% and 70 atomic% based on the total amount of silicon and aluminum were manufactured in the same manner as the comparative specimen A, except that the number of  
10 silicon chips was changed. <sup>In Table 1,</sup> symbol "o" indicates that a microstructure in which aluminum columnar structures were dispersed in a silicon area was obtained and "x" indicates that such a microstructure was not obtained. The amount of silicon is  
15 preferably 30 to 60 atomic% in terms of the uniformity of the columnar structures. When the amount of silicon is 65 or 70 atomic%, aluminum had low crystallinity and was almost amorphous.

20

25

Table 1

Amount of silicon (atomic%)	Microstructure
15 (comparative specimen A)	×
20	○
25	○
35	○
50	○
55	○
60	○
65	○
70	○
75 (Comparative specimen B)	×

A structure in which aluminum columnar structures are dispersed in a silicon area can be *achieved* realized by adjusting the amount of silicon to 20 to 70 atomic% based on the total of aluminum and silicon. By changing the ratio of aluminum and silicon, the diameter of each columnar structure can be controlled, thereby making it possible to manufacture *thin, highly linear* aluminum ~~thin wires having high linearity~~. TEM (transmission electron microscope) may be used besides SEM to identify the structure.

Further, an aluminum-silicon mixed film containing silicon in an amount of 55 atomic% based on the total amount of silicon and aluminum was formed on a glass substrate to a thickness of about 200 nm by sputtering as a comparative specimen C. A 4-inch aluminum target having eight 15 mm-square silicon chips 13 mounted thereon was used as the target. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa, and the input power was 1 kW. The substrate temperature was 350°C.

The comparative specimen C was observed through FE-SEM (field emission scanning electron microscope). When the surface of the specimen was ~~seen~~<sup>viewed</sup> from above ~~seen~~<sup>observed</sup> the substrate, large aluminum blocks could be ~~seen~~<sup>observed</sup>. It was confirmed by X-ray diffraction measurement that silicon was crystallized. That is, columnar aluminum nano-structures could not be identified and the silicon area was not amorphous but crystallized. That is, when the substrate temperature is too high, film growth for forming the above aluminum nano-structures is impossible, because aluminum ~~turns into~~<sup>becomes</sup> a more stable ~~state~~.

In order to obtain a structure having columnar members dispersed therein, it is preferred to set the Al/Si ratio of the target to 55:45.

The case where aluminum was used as the first

material and silicon was used as the second material has been described. The same result was obtained when the above-described materials, which can be used as the first or second material, were used.

5        The porous material and the production process thereof according to the present invention making use of the above structure <sup>U</sup> ~~will be described hereinafter.~~ <sup>below</sup>

(3) <sup>P</sup>orous <sup>M</sup>aterial of the <sup>P</sup>resent <sup>I</sup>nvention

10        The porous material of the present invention has a plurality of columnar pores and an area surrounding the pores. The area is an amorphous area containing C, Si, Ge or a combination thereof.

15        In Fig. 1A, reference numeral 1 denotes a plurality of columnar pores; and 2, an area surrounding them (formed from C, Si, Ge or a combination thereof). Denoted by reference numeral 3 is a substrate. Fig. 1B is a schematic sectional view <sup>along</sup> ~~cut on~~ broken line 1B-1B in Fig. 1A of the porous material.

20        As shown in Fig. 1B, according to the present invention, a porous material having substantially unbranched pores is obtained. <sup>can be observed in</sup> ~~As obvious from~~ Fig. 1B, the pores are independent from one another and perpendicular or almost perpendicular to the film surface (or substrate).

25

According to the present invention, the average interval between the centers of adjacent pores ( $2R$  in

Fig. 1B) can be set to 30 nm or less and the average diameter of the columnar pores can be set to 20 nm or less ( $2r$  in Fig. 1B). Preferably, the pore diameter  $2r$  is 0.5 to 15 nm, and the interval  $2R$  between the  
5 centers of adjacent pores is 5 to 20 nm. The length  $L$  is 0.5 nm to several micrometers, preferably 2 nm to 5  $\mu\text{m}$ . The average diameter of the pores means the average diameter of long axes obtained by processing (picking out) an image of <sup>the</sup> pores observed from the  
10 actual SEM photo (about 100 nm  $\times$  100 nm) <sup>using</sup> ~~with~~ a computer and analyzing the image based on the assumption that the pores are oval.

The pores in the porous material of the present invention can be directly connected to the substrate  
15 as shown in Fig. 1B. The present invention is not limited to this, <sup>structure,</sup> and the pores <sup>are</sup> ~~may~~ <sup>necessarily</sup> not be connected to the substrate.

The area 2 forming the porous material of the present invention contains the second material as the  
20 main component, but it may contain other elements, such as aluminum (Al), oxygen (O) and argon (Ar) in an amount of several to several tens of atomic%. In particular, when a columnar member containing the above first material, such as aluminum, is present at a  
25 position where a columnar pore is present, aluminum and the like are present in the porous material. The concentration of the first material forming the

columnar members is high near the wall surface of each pore of the porous material and low in the interior of the wall of the pore. That is, the first material contained in the porous material has a concentration distribution in the plane direction. As a matter of course, when the dispersion of the first material, such as aluminum, is promoted by heat treatment or the like, the concentration distribution of the first material is reduced.

10       The porous material is amorphous near the wall surface and in the interior of the wall of each pore.

Examples of the second material include C, Si, SiGe, Ge and a combination thereof.

15       The structure of the area 2 forming the porous material of the present invention is amorphous and the form of the pore portion, when ~~seen~~<sup>viewed</sup> from above the substrate, may be almost circular, as shown in Fig. 1A, oval, or the like.

20       The form of the pore portion forming the silicon porous material of the present invention, when ~~seen~~<sup>viewed</sup> from the section of the substrate, may be rectangular as shown in Fig. 1B, square, trapezoidal, or the like.

25       Preferably, the plurality of pores have substantially the same depth direction. The above area 2 may contain aluminum.

According to the present invention, the aspect

ratio (length/diameter) or the ratio of the length of the pore to the diameter of the pore can be set to 0.1 to 10,000.

5 The porous material of the present invention is characterized in that it is obtained by removing the first material from a structure containing the first material and the second material, the structure has columnar members containing the first material and surrounded by an amorphous area containing the second  
10 material, and the second material is contained in the structure in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material.

For example, the first material is aluminum,  
15 and the second material is Si, Ge, SiGe, C or a combination thereof.

The silicon porous material of the present invention has pores, <sup>which have</sup> ~~having~~ an average diameter of 20 nm or less and an average interval of 30 nm or less  
20 and <sup>which are</sup> ~~perpendicular~~ or almost perpendicular to the film surface. The pores are columnar, have an aspect ratio (length/diameter), which is the ratio of the length of the pore to the diameter of the pore, of 0.1 to 10,000 and are separated from one another by  
25 the silicon area containing silicon as the main component.

Fig. 1A and Fig. 1B are schematic diagrams

showing an example of the porous material of the present invention. Fig. 1A is a schematic plan view showing that pores have an average diameter of 20 nm or less and an average interval between the pores adjacent to each other is 30 nm or less, and the pores are independent from one another and are perpendicular or almost perpendicular to the film plane. Fig. 1B is a schematic sectional view cut on broken line 1B-1B of Fig. 1A of the porous material. In Fig. 1A and Fig. 1B, reference numeral 1 denotes a pore (nano-hole), 2 an area and 3 a substrate.

The porous material of the present invention is composed of the pores 1 and the area 2. The pores are separated from one another, independent from one another without being connected to one another and formed perpendicular or almost perpendicular to the substrate as shown in Fig. 1B.

The ~~form~~<sup>shape</sup> of each pore forming the porous material of the present invention is columnar as shown in Fig. 1B. The diameter  $2r$  (the average diameter of the pores, when ~~seen~~<sup>viewed</sup> from the film plane) of the pores is 20 nm or less, and the interval  $2R$  between adjacent pores (the average interval between the centers of adjacent pores, when ~~seen~~<sup>viewed</sup> from the film plane) is 30 nm or less. Preferably, the pore diameter  $2r$  is 0.5 to 15 nm and the interval  $2R$  between the centers of adjacent pores is 5 to 20 nm.



The length L is 0.5 to several micrometers,  
preferably 2 nm to 5  $\mu\text{m}$ . The average diameter of the  
pores means the average diameter of long axes  
obtained by processing (picking out) an image of pore  
5 portions observed from the actual SEM photo (about  
100 nm  $\times$  70 nm) ~~with~~ <sup>using</sup> a computer and analyzing the  
image based on the assumption that the pores are oval.

The pores in the porous material can be  
directly connected to the substrate as shown in Fig.  
10 1B. The present invention is not limited to this <sup>structure,</sup> and  
the pores ~~may~~ <sup>need</sup> not be connected to the substrate.

The area forming the porous material of the  
present invention contains silicon as the main  
component, but it may contain other elements, such as  
15 aluminum (Al), oxygen (O) and argon (Ar) in an amount  
of several to several tens of atomic%.

The structure of the porous material of the  
present invention must be amorphous. The form of the  
pore portion forming the silicon porous material of  
20 the present invention, when ~~seen~~ <sup>viewed</sup> from above the  
substrate, may be almost circular, as shown in Fig. 1A,  
oval, or the like.

The form of the pore portion forming the  
silicon porous material of the present invention, when  
25 ~~seen~~ <sup>viewed</sup> from the section of the substrate, may be  
rectangular, as shown in Fig. 1B; square, trapezoidal,  
or the like.

The aspect ratio (length/diameter), which is the ratio of the length of the pore to the diameter of the pore, is 0.1 to 10,000, preferably 0.5 to 1,000.

The present invention ~~will be~~<sup>is</sup> described hereinbelow by specifying the materials. It is to be understood that the present invention is not limited to the ~~materials to be described hereinunder.~~<sup>materials</sup>.

### (3-1) Silicon Porous Material

A silicon porous material of the present invention is a silicon porous material having columnar pores and a silicon area surrounding the pores, in which the average diameter of the pores is 20 nm or less, and the average interval between adjacent pores is 30 nm or less.

Preferably, the above porous material is a film-like silicon porous material having columnar pores and a silicon area containing silicon, in which the pores are formed perpendicular or almost perpendicular to the film plane; the average diameter of the pores is 20 nm or less; the average interval between adjacent pores is 30 nm or less; the aspect ratio (length/diameter), which is the ratio of the length of the pore to the diameter of the pore, is 0.1 to 10,000; and the pores are separated from one another by the silicon area containing silicon as the main component. An oxide film may be formed on the surface of the above silicon area.

Preferably, the average diameter of the pores is 1 to 15 nm, and the average interval between adjacent pores is 5 to 20 nm.

The above silicon area preferably contains  
5 silicon in an amount of 80 atomic% or more. ~~The~~ *This*  
amount does not include the amount of oxygen.

The above silicon area preferably contains at least silicon and aluminum.

The above silicon is preferably <sup>an</sup>amorphous  
10 silicon.

(3-2) *G*ermanium *P*orous *M*aterial

A germanium porous material of the present invention is a germanium porous material having columnar pores and a germanium area surrounding the  
15 pores, in which the average diameter of the pores is 20 nm or less, and the average interval between adjacent pores is 30 nm or less.

Preferably, the above porous material is a film-like germanium porous material having columnar  
20 pores and a germanium area containing germanium as the main component, in which the pores are formed perpendicular or almost perpendicular to the film plane; the average diameter of the pores is 20 nm or less; the average interval between adjacent pores is  
25 30 nm or less; the aspect ratio (length/diameter), which is the ratio of the length of the pore to the diameter of the pore, is 0.1 to 10,000; and the pores

are separated from one another by the germanium area containing germanium.

Preferably, the average diameter of the pores is 1 to 15 nm, and the average interval between  
5 adjacent pores is 5 to 20 nm.

The above germanium area preferably contains germanium in an amount of 80 atomic% or more. ~~This~~<sup>is</sup> amount does not include the amount of oxygen.

The above germanium area preferably contains at  
10 least germanium and aluminum.

The above germanium is preferably <sup>an</sup>amorphous germanium.

### (3-3) Silicon Germanium Porous Material

A silicon germanium porous material of the  
15 present invention is a silicon germanium porous material having columnar pores and a silicon germanium area surrounding the pores, in which the average diameter of the pores is 20 nm or less; and the average interval between adjacent pores is 30 nm  
20 or less.

Preferably, the above porous material is a film-like porous material having columnar pores and a silicon germanium area containing silicon germanium, in which the pores are formed perpendicular or almost  
25 perpendicular to the film plane; the average diameter of the pores is 20 nm or less; the average interval between adjacent pores is 30 nm or less; the aspect

ratio (length/diameter), which is the ratio of the length of the pore to the diameter of the pore, is 0.1 to 10,000; and the pores are separated from one another by the silicon germanium area containing  
5 silicon germanium as the main component.

Preferably, the average diameter of the pores is 1 to 15 nm, and the average interval between adjacent pores is 5 to 20 nm.

The above silicon germanium area preferably  
10 contains silicon and germanium in a total amount of 80 atomic% or more. This amount does not include the amount of oxygen.

The ratio of silicon (Si) to germanium (Ge) in the above silicon germanium area preferably satisfies  
15  $0 < x < 1$ , when it is expressed as  $\text{Si}_x\text{Ge}_{1-x}$ .

The above silicon germanium is preferably *an* amorphous silicon germanium.

#### (4) *Porous Material Production Process of the Present Invention*

20 A porous material production process of the present invention includes the step of preparing a structure which contains a first material and a second material in which columnar members containing the first material are surrounded by an area  
25 containing the second material (Fig. 2A) and the step of removing the columnar members from the structure (Fig. 2B). In Fig. 2A, Fig. 2B and Fig. 2C,

reference numeral 21 denotes the columnar member containing the first material; 24, the area surrounding the columnar members; 22, a substrate; 23, the structure; 25, a porous material; and 26, a pore.

5       The second material is preferably contained in the structure in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material. If a structure in which columnar structures arranged in a direction perpendicular to  
10 the substrate are dispersed in the area is obtained, the amount of the second material is not limited to the above value. In the present invention, it is important that the above structure be obtained by a combination of materials which enable the above  
15 columnar structures to be selectively removed from the structure.

As shown in Fig. 2B, after the formation of the pores, the pores can be expanded as required (Fig. 2C).

20       The above first material is, for example, aluminum or gold, and the second material is, for example, Si, SiGe, Ge, C or a combination thereof. ~~As a matter of course,~~ A plurality of different materials may be combined. The same shall apply to  
25 the following description.

In Fig. 3, the porous material production process of the present invention includes the

following steps (a) to (c).

Step (a): preparing a first material (for example, aluminum) and a second material (for example, silicon) (Fig. 3A).

5 Step (b): forming a film from the above two materials on a substrate by using a film forming process for forming a substance under a non-equilibrium condition (Fig. 3B). A structure obtained by the above process includes columnar members containing the first  
10 material and an area containing the second material ~~and~~ surrounding the columnar members. Film formation is carried out to ensure that the second material is contained in an amount of 20 to 70 atomic% based on the total amount of the first material and the second  
15 material in order to obtain a structure having columnar members dispersed therein.

Step (c): forming pores by removing the columnar members from the obtained structure (Fig. 3C). When wet etching is carried out with an acid or alkali,  
20 which can dissolve the first material more easily than the second material, the columnar members formed mainly from the first material are removed to form pores.

As for the removal of the above columnar  
25 members by etching or the like, substantially the columnar members may be selectively removed, but the columnar members do not need to be removed to the

*along*

entire length in the depth direction.

Following the above step (c), wet etching with an acid or alkali which dissolves the second material may be carried out to increase the diameters of the  
5 formed pores.

~~A description is subsequently given of the~~  
process for producing a porous material according to  
the present invention, <sup>is described below</sup> with reference to the drawings.

Fig. 4A, Fig. 4B, Fig. 4C and Fig. 4D are  
10 diagrams for explaining the process for producing a porous material according to the present invention. The process will be described in the order of the steps (a) to (d) of Fig. 4A, Fig. 4B, Fig. 4C and Fig. 4D.

15 The following steps (a) to (d) correspond to Fig. 4A, Fig. 4B, Fig. 4C and Fig. 4D, respectively. Step (a): preparing a first material (for example, aluminum) and a second material (for example, silicon) in a film forming apparatus.

20 As shown in Fig. 5, for example, chips 13 made from the second material (for example, silicon) are mounted on a target 12 (substrate) made from the first material (for example, aluminum).

Step (b): formation of a structure

25 The structure 23 is formed on the substrate 22 by a film forming process. Sputtering is used as the film forming process for forming a substance under a



non-equilibrium condition.

The structure 23 is formed on the substrate 22 by magnetron sputtering, which is the film forming process for forming a substance under a non-  
5 equilibrium condition. The structure 23 is composed of columnar members 21 containing the first material as the main component and an area 24, <sup>which</sup> <sup>S</sup> surrounding the columnar members 21 and containing <sup>S</sup> the second material as the main component.

10 With reference to Fig. 5, the process for forming a structure according to the present invention using sputtering as the process for forming a film under a non-equilibrium condition <sup>is</sup> ~~will be~~ described <sup>below</sup> ~~hereinafter~~.

15 In Fig. 5, reference numeral 11 denotes a substrate and 12 a sputtering target containing the first material. When sputtering is used, the ratio of the first material to the second material can be easily changed.

20 As shown in Fig. 5, the structure is formed on the substrate 11 by magnetron sputtering, which is the film forming process for forming a substance under a non-equilibrium condition.

The second material and the first material, as  
25 raw materials, can be prepared by placing chips 13 made from the second material on the target substrate 12 containing the first material, as shown in Fig. 5.

In Fig. 5, a plurality of chips <sup>is</sup> ~~are~~ mounted, but the present invention is not limited to this. One chip may be mounted on the target if desired film formation is possible. To disperse columnar members  
5 in the area 24 uniformly, the chips must be arranged on the substrate 12 symmetrically.

A sintered product manufactured by baking predetermined amounts of the first material powders (for example, aluminum) and the second material  
10 powders (for example, silicon) may be used as a target material for film formation.

For instance, an aluminum target and a silicon target may be separately prepared and both targets may be sputtered at the same time.

15 The amount of the second material contained in the formed film is 20 to 70 atomic%, preferably 25 to 65 atomic%, more preferably 30 to 60 atomic% based on the total amount of the first material and the second material. When the amount of the second material is  
20 within the above range, a structure having the columnar members dispersed in the area 24 is obtained.

"Atomic%" indicating the above proportion shows the proportion of the second material (for example, silicon) to the first material (for example,  
25 aluminum) in terms of the number of atoms, also expressed as "atom%" or "at%", and a value obtained by quantitatively analyzing the amounts of the two

materials in the structure by inductive coupled plasma emission spectral analysis (ICP).

"Atomic%" is used as the unit for expressing the above proportion. When wt% is used as the unit  
5 and the amount of silicon is 20 to 70 atomic%, it is 20.65 to 70.84 wt% (conversion from atomic% into wt% is carried out by obtaining the weight ratio of Al to Si on the basis that the atomic weight of Al is 26.982 and the atomic weight of Si is 28.086 and then  
10 multiplying the obtained weight ratio by the atomic% value).

The substrate temperature is 300°C or lower, preferably 200°C or lower.

When the above structure is formed by the above  
15 process, the first material and the second material become a metastable eutectic structure, whereby the first material forms nano-structures as large as several nanometers (pillar-like members) in the matrix formed from the second material and separates  
20 <sup>due</sup> ~~owing~~ to its self-organization phenomenon. The pillar-like members are almost columnar with a diameter of 1 to 20 nm and an interval of 5 to 30 nm.

The amount of the second material contained in the structure can be controlled by changing the  
25 amount of chips mounted on the target made from the first material.

When film formation is carried out under a non-

equilibrium condition, in the case of sputtering in particular, the inside pressure of a reactor is 0.2 to 1 Pa, preferably 0.1 to 1 Pa, when ~~an~~<sup>g</sup> argon gas is blown. The output for forming plasma is preferably  
5 about 150 to 1,000 W for a 4-inch target. However, the present invention is not limited to these <sup>values</sup>. Any pressure and output are acceptable, <sup>as long as</sup> if argon plasma is stably formed.

Examples of the substrate include insulating  
10 substrates, such as quartz glass and plastic substrates; semiconductor substrates, such as silicon and gallium arsenide substrates; metal substrates; carbon substrates; and substrates having one or more film layers formed thereon. The material, thickness,  
15 mechanical strength, and the like of the substrate are not particularly limited unless they are inconvenient for the formation of the structure of the present invention. The form of the substrate is not limited to a flat plate-like form, <sup>and</sup> ~~but~~ the  
20 substrate may have a curved surface or <sup>a</sup> ~~a~~ somewhat uneven or stepped surface. The form of the substrate is not particularly limited unless it is inconvenient for the structure. A flexible substrate made from a polyimide resin may also be used. In the case of a  
25 silicon substrate, a P type, N type, high-resistance or low-resistance substrate may be used.

The film forming process for forming a

substance under a non-equilibrium condition is preferably sputtering, but any film forming process for forming a substance under a non-equilibrium condition, such as resistance heating deposition or  
5 electron beam deposition (EB deposition), may be used. Sputtering is preferably carried out in such a state that plasma does not substantially contact with the substrate from which the above structure grows.

As the film forming process <sup>there</sup> may be used a  
10 simultaneous film forming process in which the first material and the second material are formed simultaneously or a laminate forming process in which several atomic-layers of both materials are formed sequentially.

15 The structure 23 formed as described above has columnar members 21 containing the first material as the main component and a silicon area 24 containing the second material as the main component ~~and~~ surrounding the columnar members.

20 The columnar members 21 contain<sup>y</sup> the first material as the main component, but may contain other elements, such as silicon, oxygen and argon, if columnar microstructures are obtained. It is desirable that the amount of the main component, for  
25 example, aluminum, is 80 atomic% or more, preferably 90 atomic% or more, in terms of the component ratio of the columnar member. This amount does not include

the amount of oxygen.

The area 24 surrounding the columnar members contains the second material as the main component, but may contain other elements, such as aluminum, oxygen and argon, if columnar microstructures are obtained. The amount of the main component (for example, the second material) is 80 atomic% or more, preferably 90 atomic% or more, in terms of the ratio of components of the area 24.

10 Step (c): formation of pores

The columnar members contained in the above structure are selectively removed. As a result, the area 24 having pores remains in the above structure to form a porous material 25.

15 The pores in the silicon porous material have an interval  $2R$  of 30 nm or less and a diameter  $2r$  of 20 nm or less, preferably a diameter  $2r$  of 1 to 15 nm and an interval  $2R$  of 5 to 20 nm. The pores have a length  $L$  of 0.5 nm to several micrometers, preferably  
20 2 to 1,000 nm.

The solution used for etching is a solution of an acid, which dissolves aluminum, but rarely dissolves silicon, such as phosphoric acid, sulfuric acid, hydrochloric acid or chromic acid. An alkali, such as  
25 sodium hydroxide, may also be used unless it is inconvenient for the formation of pores by etching. The present invention is not limited by the type of

an acid and the type of an alkali. A solution of a mixture of several acids or a mixture of several alkalis may also be used. Etching conditions, such as solution temperature, concentration and time, may be  
5 suitably selected according to a silicon porous material to be manufactured.

According to the present invention, an oxide is not formed on the whole porous material, but an oxide can be selectively formed near the surface of the  
10 wall of each pore.

Note that an oxide area can be formed on the wall of each pore of the porous material obtained through the above steps.

The following step (d) may be carried out  
15 optionally.

Step (d): expansion of pore diameter

The diameters of the pores can be suitably increased by a pore widening treatment, for example, immersing the above porous material in a solution of  
20 an acid which dissolves the second material, such as a solution of hydrogen fluoride or a solution of an alkali, such as sodium hydroxide. Any acid or alkali may be used for the solution, <sup>as long as</sup> ~~if~~ the solution has no problem with the widening of the pores. A solution  
25 of a mixture of several acids or a mixture of several alkalis may also be used.

Pore diameter expansion (pore widening)

conditions, such as solution temperature, concentration and time, can be suitably selected according to the sizes of pores to be formed.

(4-1) ~~P~~rocess for ~~P~~roducing a Silicon Porous ~~M~~aterial

5       A process for producing a silicon porous material according to the present invention includes the step of preparing an aluminum silicon structure, which contains aluminum and silicon, has columnar members containing aluminum and a silicon area  
10       surrounding the columnar members, and contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon, and the step of removing the columnar members containing aluminum from the aluminum silicon structure.

15       Preferably, the above process for producing a porous material includes (a) the step of preparing aluminum and silicon, (b) the step of forming aluminum and silicon into an aluminum silicon structure, which has columnar members containing  
20       aluminum and a silicon area surrounding the columnar members and which contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon, by using a film forming process for forming a substance under a non-equilibrium condition,  
25       and (c) the step of forming pores by etching aluminum from the aluminum silicon structure.

The etching is preferably wet etching with an



acid or alkali.

More preferably, the above process for producing a porous material includes (a) the step of preparing aluminum and silicon, (b) the step of forming aluminum and silicon into an aluminum silicon structure, which has columnar members containing aluminum and a silicon area surrounding the columnar members and which contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon, by using a film forming process for forming a substance under a non-equilibrium condition, (c) the step of forming pores by etching aluminum from the aluminum silicon structure, and (d) the step of expanding the diameters of the pores.

The step of expanding the pores is preferably wet etching with an acid or alkali.

The film forming process for forming a substance under a non-equilibrium condition is preferably sputtering.

(4-2) Process for producing a germanium porous material

A process for producing a germanium porous material according to the present invention includes the step of preparing an aluminum germanium structure, which contains aluminum and germanium, has columnar members containing aluminum and a germanium area surrounding the columnar members, and contains

germanium in an amount of 20 to 70 atomic% based on the total amount of aluminum and germanium, and the step of removing the columnar members containing aluminum from the aluminum germanium structure.

- 5            Preferably, the process for producing a porous material includes (a) the step of preparing aluminum and germanium, (b) the step of forming aluminum and germanium into an aluminum germanium structure, which has columnar members containing aluminum and a
- 10   germanium area surrounding the columnar members and which contains germanium in an amount of 20 to 70 atomic% based on the total amount of aluminum and germanium, by using a film forming process for forming a substance under a non-equilibrium condition, and
- 15   (c) the step of forming pores by etching aluminum from the aluminum germanium structure.

The etching is preferably wet etching with an acid or alkali.

- More preferably, the process for producing a
- 20   porous material includes (a) the step of preparing aluminum and germanium, (b) the step of forming aluminum and germanium into an aluminum germanium structure, which has columnar members containing aluminum and a germanium area surrounding the
- 25   columnar members and which contains germanium in an amount of 20 to 70 atomic% based on the total amount of aluminum and germanium, by using a film forming

process for forming a substance under a non-equilibrium condition, (c) the step of forming pores by etching aluminum from the aluminum germanium structure, and (d) the step of expanding the  
5 diameters of the pores.

The step of expanding the pores is preferably *carried out by* wet etching with an acid or alkali.

The film forming process for forming a substance under a non-equilibrium condition is  
10 preferably sputtering.

(4-3) *P*rocess for *P*roducing a *S*ilicon *G*ermanium  
*P*orous *M*aterial

A process for producing a silicon germanium porous material according to the present invention  
15 includes the step of preparing an aluminum silicon germanium structure, which contains aluminum, silicon and germanium, has columnar members containing aluminum and a silicon germanium area surrounding the columnar members containing aluminum, and contains  
20 silicon and germanium in a total amount of 20 to 70 atomic% based on the total amount of aluminum, silicon and germanium; and the step of removing the columnar members containing aluminum from the aluminum silicon germanium structure.

25 Preferably, the process for producing a porous material includes (a) the step of preparing aluminum, silicon and germanium, (b) the step of forming

aluminum, silicon and germanium into an aluminum silicon germanium structure, which has columnar members containing aluminum and a silicon germanium area surrounding the columnar members and which  
5 contains silicon and germanium in a total amount of 20 to 70 atomic% based on the total amount of aluminum, silicon and germanium, by using a film forming process for forming a substance under a non-equilibrium condition, and (c) the step of forming  
10 pores by etching aluminum from the aluminum silicon germanium structure.

The above etching is preferably wet etching with an acid or alkali.

More preferably, the process for producing a  
15 porous material includes (a) the step of preparing aluminum, silicon and germanium, (b) the step of forming an aluminum silicon germanium structure, which has columnar members containing aluminum and a silicon germanium area surrounding the columnar  
20 members and which contains silicon and germanium in a total amount of 20 to 70 atomic% based on the total amount of aluminum, silicon and germanium, by using a film forming process for forming a substance from aluminum, silicon and germanium under a non-  
25 equilibrium condition, (c) the step of forming pores by etching aluminum from the aluminum silicon germanium structure, and (d) the step of expanding

the diameters of the pores.

The step of expanding the pores is preferably *carried out by* wet etching with an acid or alkali.

The above film forming process for forming a  
5 substance under a non-equilibrium condition is preferably sputtering.

The proportion of the total amount of silicon and germanium to the total amount of silicon, aluminum and germanium is a value represented by  $(Si + Ge)/(Si + Ge + Al) \times 100$  (where Si is the amount of  
10 + Ge)/(Si + Ge + Al)  $\times 100$  (where Si is the amount of silicon, Ge is the amount of germanium and Al is the amount of aluminum). That is, when the total of Si + Ge + Al is 100 atomic%, it is the proportion of (Si + Ge).

15 The inventors of the present invention have conducted studies on microstructures and have ~~found~~ *made* the following finding.

*Specifically*  
~~That is,~~ they have discovered that ~~there is a case where~~ aluminum having a columnar structure is  
20 formed in a silicon matrix ~~owing to its~~ *due to the* self-formation phenomenon under predetermined conditions when silicon is added in forming an aluminum film on a substrate by using a film forming process for forming a substance under a non-equilibrium condition,  
25 such as sputtering. Then, the inventors have conducted intensive studies based on the above finding and have accomplished the present invention.

As described above, in the step of forming an aluminum silicon structure, the film forming process for forming a substance under a non-equilibrium condition is used because an aluminum silicon structure manufactured by the film forming process for forming a substance under a non-equilibrium condition has <sup>a</sup> ~~an~~ eutectic structure in which aluminum and silicon are metastable and aluminum forms nano-structures (aluminum columnar structures) having a diameter of several nanometers and separates <sup>due</sup> ~~owing~~ to ~~its self-organization phenomenon.~~

The reason why an aluminum silicon film is formed, which <sup>film</sup> contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon, is that aluminum forms columnar nano-structures only when the amount of silicon falls within the above range. That is, when the amount of silicon is <sup>less</sup> ~~smaller~~ than 20 atomic% based on the total amount of aluminum and silicon, the diameter or size of structures containing aluminum becomes larger than 20 nm and columnar members containing aluminum are not formed. When the amount of silicon is ~~larger~~ <sup>greater</sup> than 70 atomic% based on the total amount of silicon and aluminum, columnar members containing aluminum cannot be seen through an ordinary electron microscope.

In the aluminum silicon structure, only the

columnar members containing aluminum can be selectively etched with phosphoric acid, sulfuric acid or hydrochloric acid, whereby pores can be formed in silicon. The above etching is preferably  
5 wet etching with an acid or alkali.

In the process for producing a silicon porous material according to the present invention, the film forming process for forming a substance under a non-equilibrium condition is desirably sputtering. By  
10 using sputtering ~~as the film forming process for forming a substance under a non-equilibrium condition,~~ the ratio of aluminum to silicon is maintained more easily than <sup>by</sup> vacuum deposition.

The diameters of the pores (nano-hole) formed  
15 in silicon can be expanded by immersing in a solution, which dissolves silicon or silicon oxide on the surface. The step of expanding the pores is preferably wet etching with an acid or alkali.

In the present invention, the columnar members  
20 containing aluminum may also be referred to as "aluminum columnar members".

The silicon porous material according to the present invention is a silicon porous material having columnar pores and a silicon area surrounding the  
25 pores, in which the average diameter of the pores is 0.5 to 20 nm, and the average interval between adjacent pores is 30 nm or less.

The above average diameter of the pores is preferably 0.5 to 15 nm.

The average interval is preferably 20 nm or less.

5        The present invention, which has been attained by using aluminum as the first material for forming the columnar structures and silicon as the second material surrounding the columnar structures, has been described. The present invention can also be  
10        attained when the above-described material, for example, C, SiGe, Ge or a combination thereof, is used as the second material.

7Examples7

15        The following examples are provided to further illustrate the present invention.

7Example 17

      This example is a silicon porous material having pores with an average interval  $2R$  of 8 nm, an average diameter  $2r$  of 5 nm and a length  $L$  of 200 nm.

20        As shown in Fig. 4B, an aluminum silicon structure, which contained silicon in an amount of 37 atomic% based on the total amount of silicon and aluminum, was formed on a glass substrate to a thickness of about 200 nm by magnetron sputtering.  
25        Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and six 15 mm-square silicon chips mounted thereon. As for



sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 1 kW. The substrate temperature was room temperature (25°C).

5        The aluminum target having six silicon chips mounted thereon was used as the target, but the number of silicon chips is not limited to six and may be changed by sputtering conditions, so <sup>long</sup> ~~far~~ as the aluminum silicon structure has a silicon content of  
10       about 37 atomic%. The target is not limited to an aluminum target having silicon chips mounted thereon, <sup>and</sup> ~~but~~ may be a silicon target having aluminum chips mounted thereon or a target obtained by sintering silicon and aluminum.

15       The aluminum silicon structure was observed through FE-SEM (field emission scanning electron microscope). When <sup>viewed at an</sup> ~~seen~~ <sup>angle</sup> obliquely from above the substrate, the form of the surface of the structure was such that the circular columnar members  
20       containing aluminum and surrounded by a silicon area were arranged two-dimensionally as shown in Fig. 4B. The columnar members containing aluminum had a diameter of 5 nm and an average interval between the centers of 8 nm. When the sections of the columnar  
25       members were observed through FE-SEM, the columnar members had a length of 200 nm and the columnar members containing aluminum were independent from one

another.

The aluminum silicon structure containing silicon in an amount of 37 atomic% based on the total amount of silicon and aluminum was immersed in a 98% solution of concentrated sulfuric acid for 24 hours, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a silicon porous material was manufactured.

The aluminum silicon structure (silicon porous material) etched with concentrated sulfuric acid was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an angle</sup> obliquely from above the substrate, the form of the surface of the structure was such that pores 32 surrounded by an area 33 were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 5 nm and an average interval  $2R$  of about 8 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by silicon and <sup>was</sup> independent. A film was not formed between the pores and the substrate and <sup>was</sup> not observed, <sup>and</sup> the pores and the substrate were directly connected to one another.

When the manufactured specimen was measured by an X-ray diffraction method, silicon was amorphous. The amount of silicon in the silicon area was about 90 atomic% based on the total amount of silicon and

aluminum.

Silicon was used as the second material in this example, but the above process can be applied when carbon is used as the second material.

5 <sup>9</sup>Example 2<sup>9</sup>

This example is <sup>of</sup> a silicon porous material having pores with an average interval  $2R$  of 7 nm, an average diameter  $2r$  of 5 nm and a length  $L$  of 200 nm.

As shown in Fig. 4B, an aluminum silicon  
10 structure, which contained silicon in an amount of 45 atomic% based on the total amount of silicon and aluminum, was formed on a glass substrate to a thickness of about 200 nm by magnetron sputtering. Used as a target was a circular aluminum target  
15 having a diameter of 4 inches (101.6 mm) and eight 15 mm-square silicon chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 1 kW.  
20 The substrate temperature was room temperature.

The aluminum target having eight silicon chips mounted thereon was used as the target, but the number of silicon chips is not limited to eight and may be changed by sputtering conditions, so <sup>long</sup> ~~far~~ as the  
25 aluminum silicon structure has a silicon content of about 45 atomic%. The target is not limited to an aluminum target having silicon chips mounted thereon,

~~but~~ <sup>and</sup> may be a silicon target having aluminum chips mounted thereon or a target obtained by sintering silicon and aluminum.

The aluminum silicon structure was observed  
5 through FE-SEM (field emission scanning electron microscope). When seen obliquely from above the substrate, the form of the surface of the structure was such that circular aluminum columnar structures, surrounded by a silicon area were arranged two-  
10 ~~dimensionally~~ <sup>s</sup> dimensionally, as shown in Fig. 4B. The aluminum portions had an average diameter of 3 nm and an average interval of about 7 nm. When the sections of the columnar structure portions were observed through FE-SEM, the columnar structure portions had a length  
15 of 200 nm, and the columnar structure portions containing aluminum were independent from one another.

The aluminum silicon structure containing silicon in an amount of 45 atomic% based on the total amount of silicon and aluminum was immersed in a 98%  
20 solution of concentrated sulfuric acid for 24 hours, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a silicon porous material was manufactured.

The silicon porous material thus manufactured  
25 was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the

structure was such that pores surrounded by silicon were arranged two-dimensionally, as shown in Fig. 4C. The pore portions had an average diameter of about 3 nm and an average interval of about 7 nm. When the sections of the pores were observed through FE-SEM, the pores each had a length of 200 nm. The pores were independent from one another.

To expand the diameter of each pore, the silicon porous material was immersed in a 1 mol/l sodium hydroxide solution maintained at 25°C for 30 minutes.

The silicon porous material in which the diameter of each pore had been expanded was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores surrounded by a silicon area were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 5 nm and an average interval  $2R$  of 7 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by silicon and <sup>will</sup> independent. A film was not formed between the pores and the substrate, and the pores and the substrate were directly connected to one another.

When the manufactured specimen was measured by

the X-ray diffraction method, a peak showing the crystallinity of silicon could not be observed, and silicon was amorphous. The amount of silicon in the silicon area was about 90 atomic% based on the total amount of aluminum and silicon.

Example 3

This example is <sup>of</sup> a silicon porous material having pores with an average interval  $2R$  of 8 nm, an average diameter  $2r$  of 5 nm and a length  $L$  of 10 nm.

As shown in Fig. 4B, an aluminum silicon structure, which contained silicon in an amount of 37 atomic% based on the total amount of silicon and aluminum, was formed on a glass substrate to a thickness of about 10 nm by magnetron sputtering.

Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and six 15 mm-square silicon chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 1 kW. The substrate temperature was room temperature.

The aluminum target having six silicon chips mounted thereon was used as the target, but the number of silicon chips is not limited to six and may be changed by sputtering conditions, so <sup>long</sup> far as the aluminum silicon structure has a silicon content of about 37 atomic%. The target is not limited to an

aluminum target having silicon chips mounted thereon, *and*  
~~but~~ may be a silicon target having aluminum chips  
mounted thereon or a target obtained by sintering  
silicon and aluminum.

5           The aluminum silicon structure was observed  
through FE-SEM (field emission scanning electron  
microscope). When ~~seen~~ *viewed at an angle* obliquely from above the  
substrate, the form of the surface of the structure  
was such that circular columnar members containing  
10 aluminum and surrounded by a silicon area were  
arranged two-dimen<sup>s</sup>ionally, as shown in Fig. 4B. The  
columnar members containing aluminum had a diameter  
of 5 nm and an average interval between the centers  
of 8 nm. When the sections of the columnar members  
15 were observed through FE-SEM, the columnar members  
each had a length of 10 nm, and the columnar members  
containing aluminum were independent from one another.

          The aluminum silicon structure containing  
silicon in an amount of 37 atomic% based on the total  
20 amount of silicon and aluminum was immersed in a 98%  
solution of concentrated sulfuric acid for 1 hour, and  
only the aluminum columnar structure portions were  
selectively etched to form pores. As a result, a  
silicon porous material was manufactured.

25           The aluminum silicon structure (silicon porous  
material) etched with concentrated sulfuric acid was  
observed through FE-SEM (field emission scanning

electron microscope). When ~~seen~~<sup>viewed at</sup> obliquely<sup>angle</sup>, from above the substrate, the form of the surface of the structure was such that pores 32 surrounded by a silicon area 33 were arranged two-dimensionally<sup>s</sup>, as shown in Fig. 6. The pores had a diameter of 5 nm and an average interval of about 8 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 10 nm. The pores were separated from one another by the silicon area and independent. A film was not formed between the pores and the substrate, and the pores and the substrate were directly connected to one another.

When the manufactured specimen was measured by the X-ray diffraction method, a peak showing the crystallinity of silicon could not be observed and silicon was amorphous. The amount of silicon in the silicon area was about 90 atomic% based on the total amount of silicon and aluminum.

As shown in the above examples, according to the present invention, a silicon porous material having pores with an average diameter of 20 nm or less and an average interval of 30 nm or less and separated from one another by a silicon area can be formed by forming an aluminum silicon structure, which has columnar members containing aluminum and a silicon area surrounding the columnar members and which contains silicon in an amount of 20 to 70



atomic% based on the total amount of silicon and aluminum, by using a film forming process for forming a substance under a non-equilibrium condition and by selectively etching only the columnar members  
5 containing aluminum from the aluminum silicon structure.

By adjusting the amount of silicon based on the total amount of aluminum and silicon, the size of each pore and the interval between adjacent pores can  
10 be controlled, and a silicon porous material having pores perpendicular or almost perpendicular to the substrate and arranged in a large area can be manufactured.

Example 4

15 This example is a germanium porous material having pores with an average interval  $2R$  of 15 nm, an average diameter  $2r$  of 10 nm and a length  $L$  of 200 nm.

As shown in Fig. 4B, an aluminum germanium structure, which contained germanium in an amount of  
20 37 atomic% based on the total amount of silicon and germanium, was formed on a glass substrate to a thickness of about 200 nm by magnetron sputtering. Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and four 15  
25 mm-square silicon chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge

pressure was 0.7 Pa and the input power was 300 W.  
The substrate temperature was room temperature (25°C).

The aluminum target having four germanium chips mounted thereon was used as the target, but the number  
5 of germanium chips is not limited to four and may be changed by sputtering conditions, so <sup>long</sup> ~~far~~ as the aluminum germanium structure has a germanium content of about 37 atomic%. The target is not limited to an aluminum target having germanium chips mounted  
10 thereon <sup>and</sup> ~~but~~ may be a germanium target having aluminum chips mounted thereon or a target obtained by sintering germanium and aluminum powders.

The aluminum germanium structure was observed through FE-SEM (field emission scanning electron  
15 microscope). When <sup>viewed at an</sup> ~~seen~~ obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that columnar members containing aluminum, which is substantially circular in <sup>its</sup> ~~a~~ cross-section and surrounded by a silicon area were arranged two-  
20 dimensionally, as shown in Fig. 4B. The columnar members containing aluminum had a diameter of 10 nm and an average interval between the centers of 15 nm. When the sections of the columnar members were observed through FE-SEM, the columnar members had a  
25 length of 200 nm, and the columnar members containing aluminum were independent from one another.

The aluminum germanium structure containing

germanium in an amount of 37 atomic% based on the total amount of aluminum and germanium was immersed in a 98% solution of concentrated sulfuric acid for 24 hours, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a germanium porous material was manufactured.

The aluminum germanium structure (germanium porous material) etched with concentrated sulfuric acid was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores surrounded by a germanium area were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 10 nm and an average interval  $2R$  of about 15 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by germanium and were independent.

When the manufactured specimen was measured by the X-ray diffraction method, germanium was amorphous. The amount of germanium in the germanium area was about 90 atomic% based on the total amount of germanium and aluminum.

Example 5

This example is a germanium porous material having pores with an average interval  $2R$  of 15 nm, an

average diameter  $2r$  of 12 nm and a length  $L$  of 200 nm.

As shown in Fig. 4B, an aluminum germanium structure, which contained germanium in an amount of 37 atomic% based on the total amount of aluminum and germanium, was formed on a glass substrate to a thickness of about 200 nm by magnetron sputtering. Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and four 15 mm-square germanium chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 300 W. The substrate temperature was room temperature.

The aluminum target having four germanium chips mounted thereon was used as the target, but the number of germanium chips is not limited to four and may be changed by sputtering conditions, so ~~far~~<sup>long</sup> as the aluminum germanium structure has a germanium content of about 37 atomic%. The target is not limited to an aluminum target having germanium chips mounted thereon, ~~but~~<sup>and</sup> may be a germanium target having aluminum chips mounted thereon or a target obtained by sintering germanium and aluminum.

The aluminum germanium structure was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~<sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure

was such that circular aluminum columnar structures surrounded by a germanium area were arranged two-dimensionally, as shown in Fig. 4B. The aluminum portions had an average diameter of about 10 nm and an average interval of about 15 nm. When the sections of the columnar structure portions were observed through FE-SEM, the columnar structure portions had a length of 200 nm and the columnar structure portions containing aluminum were independent from one another.

The aluminum germanium structure containing germanium in an amount of 37 atomic% based on the total amount of aluminum and germanium was immersed in a 98% solution of concentrated sulfuric acid for 24 hours, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a germanium porous material was manufactured.

The germanium porous material thus manufactured was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores surrounded by germanium were arranged two-dimensionally, as shown in Fig. 4C. The pore portions had an average diameter of about 10 nm and an average interval of about 15 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were

independent from one another.

To expand the diameter of each pore, the germanium porous material was immersed in a sodium hydroxide solution having a concentration of 1 mol/l and maintained at 25°C for 15 minutes.

The germanium porous material in which the diameter of each pore had been expanded was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores 32 surrounded by a germanium area 33 were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 12 nm and an average interval  $2R$  of 15 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by germanium and <sup>were</sup> independent.

When the manufactured specimen was measured by the X-ray diffraction method, a peak showing the crystallinity of germanium could not be observed and germanium was amorphous. The amount of germanium in the germanium area was about 90 atomic% based on the total amount of aluminum and germanium.

Example 6

This example is <sup>of</sup> a germanium porous material having pores with an average interval  $2R$  of 15 nm, an average diameter  $2r$  of 10 nm and a length  $L$  of 10 nm.

As shown in Fig. 4B, an aluminum germanium structure, which contained germanium in an amount of 30 atomic% based on the total amount of aluminum and germanium, was formed on a glass substrate to a thickness of about 10 nm by magnetron sputtering. Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and three 15 mm-square germanium chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 300 W. The substrate temperature was room temperature.

The aluminum target having three germanium chips mounted thereon was used as the target, but the number of germanium chips is not limited to three and may be changed by sputtering conditions, so ~~far~~<sup>long</sup> as the aluminum germanium structure has a germanium content of about 30 atomic%. The target is not limited to an aluminum target having germanium chips mounted thereon, ~~but~~<sup>and</sup> may be a germanium target having aluminum chips mounted thereon or a target obtained by sintering germanium and aluminum.

The aluminum germanium structure was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~<sup>viewed at an</sup> obliquely ~~from~~<sup>angle</sup> above the substrate, the form of the surface of the structure was such that circular columnar members containing

aluminum and surrounded by a germanium area were arranged two-dimensionally, as shown in Fig. 4B. The aluminum nano-structure portion had a diameter of 12 nm and an average interval between the centers of 15 nm. When the sections of the columnar structure portions were observed through FE-SEM, the columnar structure portions had a length of 10 nm, and the columnar structure portions containing aluminum were independent from one another.

10        The aluminum germanium structure containing germanium in an amount of 30 atomic% based on the total amount of aluminum and germanium was immersed in a 98% solution of concentrated sulfuric acid for 12 hours and only the aluminum columnar structure  
15 portions were selectively etched to form pores. As a result, a germanium porous material was manufactured.

      The aluminum germanium structure (germanium porous material) etched with phosphoric acid was observed through FE-SEM (field emission scanning  
20 electron microscope). When ~~seen~~ <sup>viewed at an angle</sup> obliquely from above the substrate, the form of the surface of the structure was such that pores 32 surrounded by a germanium area 33 were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 12  
25 nm and an average interval  $2R$  of about 15 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 10 nm. The pores were



separated from one another by the germanium area and *was* independent.

When the manufactured specimen was measured by the X-ray diffraction method, germanium was amorphous.

- 5 The amount of germanium in the germanium area was about 90 atomic% based on the total amount of aluminum and germanium.

As shown in the above examples, according to the present invention, a germanium porous material  
10 having pores with an average diameter of 20 nm or less and an average interval of 30 nm or less and separated from one another by a germanium area can be formed by forming an aluminum germanium structure, which has columnar members containing aluminum and a  
15 germanium area surrounding the columnar members and which contains germanium in an amount of 20 to 70 atomic% based on the total amount of germanium and aluminum by using a film forming process for forming a substance under a non-equilibrium condition and by  
20 selectively etching only the columnar members containing aluminum from the aluminum germanium structure.

By adjusting the amount of germanium based on the total amount of aluminum and germanium, the size  
25 of each pore and the interval between adjacent pores can be controlled and a germanium porous material having pores perpendicular or almost perpendicular to

the substrate and arranged in a large area can be manufactured.

*9* Example 7 *r*

This example is *if* a silicon germanium porous  
5 material having pores with an average interval  $2R$  of  
10 nm, an average diameter  $2r$  of 7 nm and a length  $L$   
of 200 nm.

As shown in Fig. 4B, an aluminum silicon  
germanium structure, which contained silicon and  
10 germanium in a gross amount of 38 atomic% based on  
the total amount of aluminum, silicon, and germanium,  
was formed on a glass substrate to a thickness of  
about 200 nm by magnetron sputtering. Used as a  
target was a circular aluminum target having a  
15 diameter of 4 inches (101.6 mm) and two 15 mm-square  
germanium chips and two 15 mm-square silicon chips  
mounted thereon. As for sputtering conditions, an RF  
power source was used, the flow rate of Ar was 50  
sccm, the discharge pressure was 0.7 Pa and the input  
20 power was 300 W. The substrate temperature was room  
temperature (25°C).

The aluminum target having two silicon chips  
and two germanium chips mounted thereon was used as  
the target, but the number of silicon chips and  
25 germanium chips is not limited thereto and may be  
changed by sputtering conditions, so *long* far as the  
aluminum silicon germanium structure has a silicon

germanium content of about 38 atomic%. The target is not limited to an aluminum target having silicon chips and germanium chips mounted thereon, <sup>and</sup> ~~but~~ may be a silicon target having germanium chips and aluminum chips mounted thereon, a germanium target having silicon chips and aluminum chips mounted thereon, or a target obtained by sintering silicon, germanium, and aluminum powders.

The aluminum silicon germanium structure was observed through FE-SEM (field emission scanning electron microscope). When <sup>viewed at an</sup> ~~seen~~ obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that columnar members containing aluminum, which <sup>have</sup> ~~is~~ substantially circular ~~in~~ cross-section and <sup>are</sup> ~~surrounded~~ by a silicon germanium area, were arranged two-dimensionally, as shown in Fig. 4B. The columnar members containing aluminum had a diameter of 7 nm and an average interval between the centers of 10 nm. When the sections of the columnar members were observed through FE-SEM, the columnar members had a length of 200 nm and the columnar members containing aluminum were independent from one another.

The aluminum silicon germanium structure containing silicon and germanium in a gross amount of 38 atomic% based on the total amount of aluminum, silicon, and germanium was immersed in a 98% solution

of concentrated sulfuric acid for 24 hours and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a silicon germanium porous material was manufactured.

5           The aluminum silicon germanium structure (silicon germanium porous material) etched with concentrated sulfuric acid was observed through FE-SEM (field emission scanning electron microscope).  
When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the  
10 form of the surface of the structure was such that pores 32 surrounded by a silicon germanium area 33 were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 7 nm and an average interval  $2R$  of about 10 nm. When the sections of the  
15 pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by a mixture of silicon and germanium and ~~was~~ independent.

When the manufactured specimen was measured by  
20 the X-ray diffraction method, silicon germanium (mixture member of silicon and germanium) was amorphous. The gross amount of silicon germanium in the silicon germanium area was about 90 atomic% based on the total amount of silicon, germanium, and  
25 aluminum.

Example 8

This example is a silicon germanium porous

material having pores with an average interval  $2R$  of 10 nm, an average diameter  $2r$  of 8 nm and a length  $L$  of 10 nm.

As shown in Fig. 4B, an aluminum silicon  
5 germanium structure, which contained silicon and germanium in a gross amount of 38 atomic% based on the total amount of aluminum, silicon, and germanium, was formed on a glass substrate to a thickness of about 200 nm by magnetron sputtering. Used as a  
10 target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and two 15 mm-square silicon chips and two 15 mm-square germanium chips mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50  
15 sccm, the discharge pressure was 0.7 Pa and the input power was 300 W. The substrate temperature was room temperature.

The aluminum target having two silicon chips and two germanium chips mounted thereon was used as  
20 the target, but the number of silicon chips and germanium chips is not limited thereto and may be changed by sputtering conditions, so <sup>long</sup> far as the aluminum silicon germanium structure has a silicon germanium content of about 38 atomic%.

25 The target is not limited to an aluminum target having silicon chips and germanium chips mounted thereon, <sup>and</sup> but may be a silicon target having germanium

chips and aluminum chips mounted thereon, a germanium target having silicon chips and aluminum chips mounted thereon, or a target obtained by sintering silicon, germanium, and aluminum powders.

5        The aluminum silicon germanium structure was observed through FE-SEM (field emission scanning electron microscope). When <sup>viewed at an angle</sup> ~~seen~~ obliquely from above the substrate, the form of the surface of the structure was such that circular aluminum columnar  
10 structures surrounded by a silicon germanium area were arranged two-dimensionally, as shown in Fig. 4B. The aluminum portions had an average diameter of 7 nm and an average interval between the centers of 10 nm. When the sections of the columnar members were  
15 observed through FE-SEM, the columnar members had a length of 200 nm and the columnar members containing aluminum were independent from one another.

      The aluminum silicon germanium structure containing silicon and germanium in a gross amount of  
20 38 atomic% based on the total amount of aluminum, silicon, and germanium was immersed in a 98% solution of concentrated sulfuric acid for 24 hours, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a  
25 silicon germanium porous material was manufactured.

      The silicon germanium porous material thus manufactured was observed through FE-SEM (field

emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores surrounded by silicon germanium were arranged two-dimensionally, as shown in Fig. 4C. The pore portions had an average diameter of about 7 nm and an average interval of about 10 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were independent from one another.

To expand the diameter of each pore, the silicon porous material was immersed in a sodium hydroxide solution having a concentration of 1 mol/l and maintained at 25°C for 10 minutes.

The silicon germanium porous material in which the diameter of each pore had been expanded was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that pores surrounded by a silicon germanium area were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter  $2r$  of 8 nm and an average interval  $2R$  of 10 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 200 nm. The pores were separated from one another by silicon germanium and independent.

When the manufactured specimen was measured by the X-ray diffraction method, silicon germanium (mixture member of silicon and germanium) was amorphous. The gross amount of silicon and germanium in the silicon germanium area was about 90 atomic% based on the total amount of silicon, germanium, and aluminum.

Example 9

This example is a silicon germanium porous material having pores with an average interval  $2R$  of 8 nm, an average diameter  $2r$  of 6 nm and a length  $L$  of 10 nm.

As shown in Fig. 4B, an aluminum silicon germanium structure, which contained silicon and germanium in a gross amount of 33 atomic% based on the total amount of aluminum, silicon, and germanium, was formed on a glass substrate to a thickness of about 10 nm by magnetron sputtering. Used as a target was a circular aluminum target having a diameter of 4 inches (101.6 mm) and three 15 mm-square silicon chips and one 15 mm-square germanium chip mounted thereon. As for sputtering conditions, an RF power source was used, the flow rate of Ar was 50 sccm, the discharge pressure was 0.7 Pa and the input power was 300 W. The substrate temperature was room temperature.

The aluminum target having three silicon chips



and one germanium chips<sup>✓</sup> mounted thereon was used as the target but the number of silicon chips and germanium chips is not limited thereto and may be changed by sputtering conditions so far as the  
5 aluminum silicon germanium structure has a silicon germanium content of about 33 atomic% in film formation.

The target is not limited to an aluminum target having silicon chips and germanium chips mounted  
10 thereon, but may be a silicon target having germanium chips and aluminum chips mounted thereon, a germanium target having silicon chips and aluminum chips mounted thereon, or a target obtained by sintering silicon, germanium, and aluminum powders.

15 The aluminum silicon germanium structure was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an</sup> obliquely <sup>angle</sup> from above the substrate, the form of the surface of the structure was such that circular columnar members  
20 containing aluminum and surrounded by a silicon germanium area were arranged two-dimen<sup>s</sup>ionally, as shown in Fig. 4B. The aluminum nano-structure portion had a diameter of 6 nm and an average interval between the centers of 10 nm. When the  
25 sections of the columnar members were observed through FE-SEM, the columnar members had a length of 200 nm and the aluminum columnar structure portions

were independent from one another.

The aluminum silicon germanium structure containing silicon and germanium in a gross amount of 33 atomic% based on the total amount of aluminum, silicon, and germanium was immersed in a 98% solution of concentrated sulfuric acid for 1 hour, and only the aluminum columnar structure portions were selectively etched to form pores. As a result, a silicon germanium porous material was manufactured.

10. The aluminum silicon germanium structure (silicon germanium porous material) etched with concentrated sulfuric acid was observed through FE-SEM (field emission scanning electron microscope). When ~~seen~~ <sup>viewed at an angle</sup> obliquely from above the substrate, the form of the surface of the structure was such that pores 32 surrounded by a silicon germanium area 33 were arranged two-dimensionally, as shown in Fig. 6. The pores had a diameter of 6 nm and an average interval of about 8 nm. When the sections of the pores were observed through FE-SEM, the pores had a length of 10 nm. The pores were separated from one another by the silicon germanium area and <sup>were</sup> independent.

- 25 When the manufactured specimen was measured by the X-ray diffraction method, silicon germanium was amorphous. The gross amount of silicon and germanium in the silicon germanium area was about 90 atomic% based on the total amount of silicon, germanium, and

aluminum.

As shown in the above examples, according to the present invention, a silicon germanium porous material having pores with an average diameter of 20  
5 nm or less and an average interval of 30 nm or less and separated from one another by a silicon germanium area can be formed by forming an aluminum silicon germanium structure, which has columnar members containing aluminum and a silicon germanium area  
10 surrounding the columnar members and which contains silicon and germanium in a gross amount of 20 to 70 atomic% based on the total amount of aluminum, silicon, and germanium, by using a film forming process for forming a substance under a non-  
15 equilibrium condition and by selectively etching only the columnar members containing aluminum from the aluminum silicon germanium structure.

By adjusting the amount of silicon germanium based on the total amount of aluminum, silicon, and  
20 germanium, the size of each pore and the interval between adjacent pores can be controlled, and a silicon germanium porous material having pores perpendicular or almost perpendicular to the substrate and arranged in a large area can be  
25 manufactured.

The present invention makes it possible to apply pores contained in silicon, germanium and

silicon germanium in various forms, thereby greatly expanding their applicable uses. For example, the silicon, germanium and silicon germanium porous bodies of the present invention can be used as a functional material ~~for such as~~ <sup>IM</sup> light-emitting devices, optical devices and microdevices. They can also be used as a base material or mold for novel nano-structures. Further, they can also be used as a filter or etching mask.

10 ~~/~~Effect of the Invention~~/~~

As described above, according to the present invention, there can be provided a novel porous material and a production process thereof.

WHAT IS CLAIMED IS:

1. A porous material comprising a plurality of columnar pores and an area surrounding the pores, the area being an amorphous area containing C, Si, Ge or  
5 a combination thereof.

2. A porous material according to claim 1, wherein the columnar pores are substantially unbranched.  
10

3. A porous material according to claim 1, wherein the average interval between the centers of adjacent pores is 30 nm or less.

4. A porous material according to claim 1, wherein the average diameter of the columnar pores is 20 nm or less.  
15

5. A porous material according to claim 1, wherein the plurality of pores have substantially the same depth direction.  
20

6. A porous material according to claim 1, wherein the area contains aluminum.

7. A porous material according to any one of claims 1 to 6, wherein the porous material is formed  
25

on a substrate and the depth directions of the columnar pores are substantially perpendicular to the substrate.

5        8. A porous material obtained by removing a first material from a structure comprising the first material and a second material, wherein the structure has columnar members containing the first material and surrounded by an amorphous area containing the  
10       second material and contains the second material in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material.

15       9. A porous material according to claim 8, wherein the first material is aluminum.

20       10. A porous material according to claim 8, wherein the second material is Si, Ge, SiGe, C or a combination thereof.

25       11. A porous material according to claim 8, wherein the average interval between the centers of adjacent pores is 30 nm or less.

30       12. A porous material according to claim 8, wherein the diameter of the columnar pores is 20 nm or less.

13. A process for producing a porous material comprising the steps of:

preparing a structure which comprises a first material and a second material and has columnar members containing the first material and surrounded by an area containing the second material; and removing the columnar members from the structure.

10 14. A process for producing a porous material according to claim 13, wherein the structure contains the second material in an amount of 20 to 70 atomic% based on the total amount of the first material and the second material.

15 15. A process for producing a porous material according to claim 14, wherein the first material contains aluminum.

20 16. A process for producing a porous material according to claim 14, wherein the second material contains C, Si, Ge, SiGe or a combination thereof.

25 17. A process for producing a porous material according to claim 13, wherein the structure is formed by using a process for forming a film under a non-equilibrium condition.

18. A process for producing a porous material according to claim 13, wherein the removing step is wet etching with an acid or alkali.

5 19. A process for producing a porous material according to claim 13, further comprising after the removing step the step of expanding the diameters of pores formed by the removing step.

10 20. A process for producing a porous material according to any one of claims 13 to 19, wherein the columnar members have a diameter of 20 nm or less and an average interval between their centers of 30 nm or less.

15 21. A process for producing a porous material comprising the steps of:  
preparing a structure which comprises aluminum and silicon, has columnar members containing aluminum  
20 and a silicon area surrounding the columnar members, and contains silicon in an amount of 20 to 70 atomic% based on the total amount of aluminum and silicon;  
and

25 removing the columnar members from the structure.

22. A process for producing a porous material



according to claim 21, wherein the silicon area contains germanium..

23. A filter comprising the porous material of  
5 claim 1 or 8.

24. A mask material comprising the porous  
material of claim 1 or 8.

ABSTRACT OF THE DISCLOSURE

There are provided a porous material and a process for producing the same. The porous material has a plurality of columnar pores and an area surrounding the pores, and the area is an amorphous area containing C, Si, Ge or a combination thereof.

5